

# The Diagnostics of the Chemical Reaction Zone at the Detonation of Condensed Explosives

Nataliya P. Satonkina\*

(Dated: October 11, 2016)

The highly-sensitive method is proposed for the real-time diagnostics of the chemical peak (von Neumann peak) at detonation of brisant high explosives. The absence of the direct link between the pressure and the course of chemical reactions was shown. For TNT, the influence of the structure of charge on the kinetics of chemical peak was demonstrated.

PACS numbers: 82.33.Vx, 82.40.Fp, 82.60.Qr

## I. INTRODUCTION

According to the Zeldovich – von Neumann – Döring (ZND) theory, detonation wave consists of the thin (several intermolecular distances) shock wave region, the chemical reaction zone, the Chapman – Jouguet plane (CJ point in one-dimensional case), and the Taylor rarefaction wave. It is commonly accepted that the CJ point which divided the regions of subsonic and supersonic flows corresponds to the ending of the chemical reaction zone. However, a strict validation of the link between the ending of the chemical peak and the CJ point is absent. Since the chemical peak in the ZND model is defined as a region of high pressure, it is investigated solely using the time dependencies of the pressure obtained directly or indirectly by the measurement of mass velocity and temperature. Many authors note the difficulty to set the CJ point which is explained, for example, by an incomplete chemical reaction.

Data on the duration of the chemical peak show large scatter (for a review see [1]) as well as the different dependence on the charge configuration, density, length and diameter. This could be due to the absence of the universal way to find the singularity (the kink point) at the pressure profile, and also it indicates the methodical difficulties.

Neither density nor pressure give the direct information on the chemical composition of the matter. Zeldovich and Kompaneets noted in their book on the detonation theory [2] that the detonation velocity, the mass velocity of the explosion products, and the pressure do not depend on the speed of the chemical reaction. This means the absence of the relation between the duration of chemical reaction and mechanic parameters.

As shown in the works [3, 6–10], high electric conductivity at the detonation of condensed HEs with negative oxygen balance is related to the presence of carbon. In the works [9, 10], the link between the value of conductivity and the mass fraction of carbon is shown for the

whole detonation wave. Based on these results, we propose in this paper a new method for the diagnostics of the state of the matter in the von Neumann peak based on the electric conductivity profile.

### Results of the investigation of the duration of the pressure peak

The duration of the chemical peak was investigated earlier in the works [1, 3, 6, 7].

The increase of the chemical peak duration  $\Delta t$  with an increase of the TATB charge diameter was obtained in the work of Loboiko [1] using the registration of the light emission from the shock wave in chloroform. There was also an influence of the charge length, for RDX,  $\Delta t$  increased with the increase of the length at constant diameter. Authors note that there is no clearly defined boundary between the reaction zone and the Taylor wave. They interpret this as an indirect evidence of the incompleteness of chemical reactions. The duration of the chemical peak was determined using the averaging of pressure profiles from several experiments followed by the smoothing and taking the logarithm. This procedure gave two straight lines in semilogarithmic coordinates. The intersection of these lines was taken as the CJ point.

In the work of Fedorov [3], the detonation parameters and the density profiles for individual and mixed HEs were obtained by the Fabry – Pérot method with the nanosecond resolution. From these profiles, the pressure in the von Neumann peak, the CJ point and the duration of the chemical peak were determined. Besides the common pressure profiles with a kink corresponding to the CJ point, the smooth profiles were obtained as well as the nonmonotonic profiles with two kinks. For HEs of powder density, profiles with large oscillations caused by the high degree of nonuniformity were also observed. The duration of the chemical peak increased with the increase of the charge size.

In the work of Dreminev [6], the increase of  $\Delta t$  with the decrease of density was obtained for TNT and RDX by the magnetoelectric method of the mass velocity registration. For RDX [6], the duration increased from 100 ns for the density of  $\rho = 1.72 \text{ g/cm}^3$  to 400 ns ( $\rho = 0.95 \text{ g/cm}^3$ ). Less pronounced increase of the duration by 20% with the increase of the charge diameter from 18 mm to 40 mm with the fixed density of  $\rho = 1.00 \text{ g/cm}^3$  was also observed.

\*Lavrentyev Institute of Hydrodynamics, Novosibirsk, 630090 Russia  
Novosibirsk State University, Novosibirsk, 630090 Russia; Electronic address: snp@hydro.nsc.ru

TABLE I: Data on the duration of the chemical peak

HE	$\rho$ , g/cm <sup>3</sup>	$\Delta t$ , ns	ref
TNT press.1	1.53	190	[1]
TNT press.2	1.62	330	[1]
TNT cast	1.56	290	[1]
TNT	1.62	305	[3]
TNT	1.62	260÷360	[6]
RDX	1.44	200	[6]
RDX	1.68	50÷70	[1]
RDX	1.72	≤100	[6]
PETN	1.73	80	[1]
PETN	1.74	5	[1]
PETN		25	[8]
HMX	1.86	60	[1]
HMX	1.90	40	[1]
HMX		30	[8]

Results of recent works listed are summarized in the Table 1. Maximum and minimum values for PETN differ by the factor 16. The paper [23] contain the data for several HEs. The values obtained for the same density by different methods differ by several times.

In the work of Titov[7], the size of nanodiamonds obtained in the explosion of cylindrical and spherical charges of the same composition with different initiation methods was investigated. No dependence was found, which led to the conclusion that nanodiamonds form in the chemical peak with parameters independent on the geometry.

Thus, there is no common pattern in the influence of the HE density on  $\Delta t$  with a visible link to the charge geometry and configuration, the presence and the sort on a shell. The large scatter of data is observed related primarily to the method of determining the CJ point.

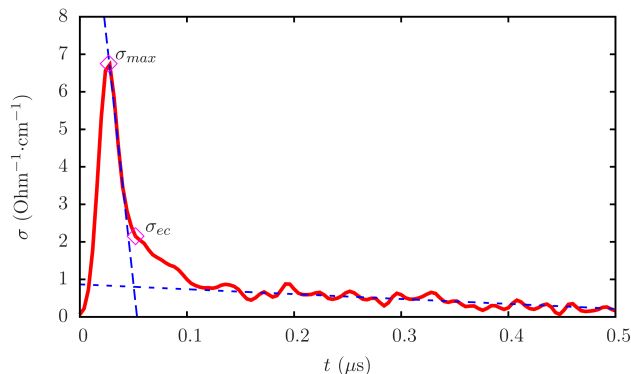


FIG. 1: Conductivity profile at the detonation of condensed HE.

### Methodology

A typical conductivity profile  $\sigma(t)$  at the detonation of condensed HEs with slightly negative oxygen balance is shown in Fig. 1. The conductivity increases to the

maximum value  $\sigma_{max}$  in several nanoseconds, and later decreases until the point labelled  $\sigma_{ec}$ . The gradient of this decrease depends on the HE. The method for the determining the duration of the conductivity peak by an intersection of two approximating straight lines is shown. In the papers [9, 10], the value of  $\sigma_{max}$  is related to the total carbon content in the HE, and the value of  $\sigma_{ec}$  is related to the content of the condensed carbon which is calculated using the BKW equation (the data of [11]) for the CJ point under the assumption that the CJ point coincides with the ending of chemical reactions. The given dependence of the conductivity  $\sigma$  on the carbon content for the mass fraction of carbon from 0 to 0.37 is universal for five HEs.[9, 10] This indicates the crucial role of the carbon for the conductivity process in the chemical peak and in the whole detonation wave.

We assume that the high conductivity at the detonation is provided by the contact mechanism along the connected highly-conductive carbon nanostructures. The conductivity of carbon varies in a wide range from 240 to 1250 Ohm<sup>-1</sup>cm<sup>-1</sup>. The conductivity of highly oriented graphite can be as high as  $2 \cdot 10^4$  Ohm<sup>-1</sup>cm<sup>-1</sup> [12, 13].

In such HEs as PETN, HMX, RDX, the mass fraction of carbon in the molecule is higher than 0.15 which is sufficient for the formation of elongated structures. In the region where the chemical reaction ends, the carbon fraction is lower than 0.07 which is not sufficient for contact conductivity as shown in [14]. Because of such difference, the reaction zone is distinctly pronounced in the conductivity graph. In carbon-rich HEs such as TNT and TATB, the amount of carbon is sufficient for the formation of "wires" both in the maximum and in the point of  $\sigma_{ec}$ . Therefore, the chemical peak is resolved only at the decrease of the density to powder values [15, 16, 28].

The existence of carbon nets is confirmed in following sources. In the work [18], it was shown that the formation of the carbon structures can not proceed through the intermediate release of a free carbon. A mechanism of nanodiamond formation was proposed related to the partial breaking of molecular bonds and the formation and growth of carbon framework. The author of [19, 20] based on the experiments with isotope label claims that the oxidation of carbon occurs later than the formation of carbon particles, and confirms fast clustering of carbon atoms. This agrees with the data listed. In the works of Gilev [4, 5], it was shown that high maximal conductivity of 250 Ohm<sup>-1</sup>cm<sup>-1</sup> at the detonation of TNT can not be explained by the percolation conductivity because even the total carbon content is insufficient, and the elongated structures with almost metallic conductivity should be formed. The carbon clustering at heating of molecules of TATB, HMX and RDX was investigated in [8] using the molecular dynamics method. The carbon nanostructures were obtained which agrees well with their presence already in the reaction zone. The conclusions were made that the higher content of carbon decreases the HE sensitivity and increases the stability of a carbon cluster which hinders the chemical reaction and increases its duration.

The additional indirect confirmation of the presence of elongated "wires" are the observation of the formation of carbon structures under different conditions [30–33] and the carbon filaments found in the detonation products [34–36].

Thus, the electric conductivity traces the state of carbon. Before the arrival of the detonation front, HE is dielectric, and all carbon is bound in molecules. The conductivity in the shock front is insignificant. The peak region (Fig. 1) can be divided into three parts. The conductivity increase to the maximum corresponds to the decay of initial HE molecules accompanied by the growth of carbon structures. The oxidation of carbon occurs between the points  $\sigma_{max}$  and  $\sigma_{ec}$  leading to the thinning and partial breaking of conductive structures which results in the decrease of the conductivity. The transition region between 0.05 and 0.1  $\mu s$  could be caused by the decrease of the intensity of oxidation reactions due to the decrease of concentrations of reactive components. This transition region is observed on the profiles for all HEs at high density, and it is weakly pronounced at powder densities. The region of  $t > 0.1 \mu s$  corresponds to the Taylor wave.

We define the ending of the chemical peak as the place within the detonation wave where the decay of initial HE molecules is finished, and the synthesis of main products which constitute more than 97% of the detonation products (C, CO, CO<sub>2</sub>, N<sub>2</sub>, H<sub>2</sub>O) already occurs. This point corresponds to the place of  $\sigma_{ec}$  in Fig. 1. The change of the chemical composition[11] due to the pressure decrease and the shift of the chemical equilibrium (which is formally also a chemical reaction) corresponds to the Taylor wave.

### Results of investigation of electric conductivity

The experimental data used for the analysis were obtained by the high-resolution scheme described in detail in the work of Ershov[21]. HE was placed inside a thick-walled copper cylinder with inner diameter of 8 mm. Such shell decreases the critical diameter by 6–8 times [22] ensuring the steady detonation. The diameter used was much larger than the critical one for RDX, PETN and HMX.

The data on the duration of the conductivity peak for RDX, PETN and HMX at different densities are shown in Fig. 2. The scatter of values is due to the high sensitivity of the method. The maximum difference of the front arrival related to the constructive features of the scheme used is 0.27 mm which corresponds to  $\sim 50$  ns. Therefore, there is an inherent probability of the widening of the signal peak. The difference between maximum and minimum values for densities larger than 1.4 g/cm<sup>3</sup> corresponds to this estimate, hence, the minimal obtained values should be considered. One can claim that there is no noticeable density dependence of the conductivity peak duration (the influence of the density on the chemical peak duration). Since the data shown in Fig. 2 were obtained at the same geometric charge parameters for different densities, this indicates to the absence of direct

link between the density profile and the chemical reaction zone.

At powder densities ( $\rho < 1.4$  g/cm<sup>3</sup>, data of Ershov[24]), a fundamental change of the conductivity profile occurs at a certain grain size specific for the type HE. The oscillation arise with a spatial size four times smaller than the grain size. Such correlations were observed for PETN (260 and 80  $\mu m$ ) and for HMX (460  $\mu m$ ). The profiles for HMX (21  $\mu m$ ) and RDX (160 and 11  $\mu m$ ) are qualitatively the same as for higher densities. The peculiarities for low-density HEs were observed in the pressure profiles for HMX in the work of Fedorov[25] and for PETN in the work Ershov[26]. This was related to the non-classical detonation regime of the detonation propagation driven by jets. As a result, the front is highly curved, there is the reacted as well as the initial matter within the same cross-section. This influence measurements of electric conductivity because electric field force lines become curved, and the averaging is performed based on the minimization of the electric resistance rather than along the cross-section. Nevertheless, the influence of the grain size on the reaction zone was registered by the electric conductivity method. The decrease of the conductivity peak duration with the decrease of the grain size was observed in [24] which first of all reflects the influence of the degree of non-uniformity of the initial charge structure.

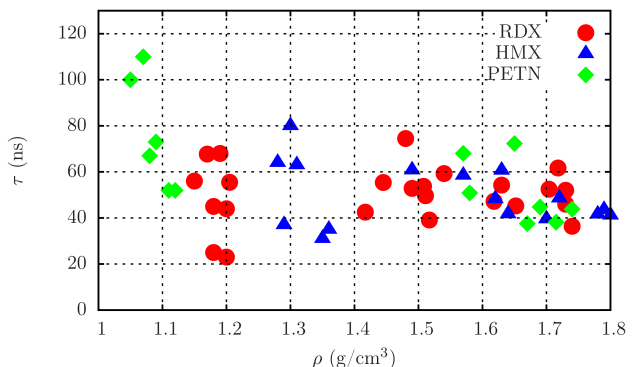


FIG. 2: The duration of the conductivity peak at the detonation of RDX, HMX at PETN at different density, data [21, 24].

The kinetics of chemical reactions should be independent on the charge diameter and length. The charge geometry however influence the rarefaction. The data on the duration of the chemical peak obtained from the pressure profile correspond to the decrease of thermodynamic parameters, whereas the duration of the reaction zone is governed solely by the chemical reaction of the ignition and burning from initial points related to the hot spot theory. This can explain the independence on the density.

Considering electric conductivity to be due to carbon nanostructures and taking into account that the maximum value is connected with the total carbon content,

and the value in the CJ point – to the condensed carbon content, we get a tool to investigate the chemical reaction zone. The duration of the conductivity peak defines the duration of the chemical reaction zone. Note that the width of the conductivity peak increases with the increase of the density and, correspondingly, of the detonation velocity.

### Diagnosics of the chemical reaction at the detonation of TNT

Different parameters for cast and pressed TNT are noted in literature. Different duration of the pressure peak (see Table 1) and the three- to tenfold difference of the critical diameter is related to different character of nonuniformities dependent of the details of charge preparation.

It is commonly assumed the the hot spots are generated at the nonuniformities, and the chemical reaction proceeds from these spots. The strong influence of the concentration of hot spots on the reaction time was shown in the work [27]. For HMS and PETN, the duration of the pressure peak in single crystals was several times larger comparing to smaller densities. The role of hot spots in TNT can be traced using conductivity profiles.

The maximum conductivity of  $\sim 25 \text{ Ohm}^{-1}\text{cm}^{-1}$  at the detonation of cast TNT was obtained in the work [29]. For TNT pressed to the density of  $1.57 \text{ g/cm}^3$ , the conductivity of  $100 \text{ Ohm}^{-1}\text{cm}^{-1}$  was obtained in [28]. The values of conductivity for pressed TNT is three times higher whereas the values of detonation velocity, pressure and density differ only slightly. The character of conductivity profiles also differs significantly. In the pressed TNT, a fast increase of the conductivity up to a maximum value was observed with a following weak decrease. For the cast TNT, the gradient of the increase is considerably smaller, and the value of conductivity remains the same for about  $1 \mu\text{s}$ . Using the notion of hot spots this can be explained as following.

In pressed TNT, hot planes are produced at the contact of grains, and the reaction proceeds there. In cast TNT at relatively low concentration of pores of the size near  $0.1 \text{ mm}$  or at the presence of significantly larger pores, the time of burning until the overlap of reacting regions is sufficiently higher. Not only the destruction of initial molecules but also the synthesis of main reaction products have time to occur in the reacting regions. Thus, the matter reacted up to different stages (from the initial one to fully reacted) is present in the cross-section where the measurement is made. In such case, the magnitude of conductivity is limited by the amount of condensed carbon which is observed. Hence, the course of the chemical

reaction in cast and pressed TNT is essentially different even at close detonation parameters. This is successfully detected by the electric conductivity.

### Conclusions

A new method was proposed for the diagnostics of the state of matter in the chemical peak region. The method is based on the link between the magnitude of electric conductivity and the amount of carbon condensed to nanostructures.

The spatial distribution of conductivity provides the real-time information by the tracing the carbon transition from a non-conductive state to a conductive one.

The sensitivity of the diagnostics was demonstrated in such phenomena as the influence of the HE grain size on the peak duration at powder density, the jet mechanism of the detonation propagation. The role of hot spots in the kinetics of chemical reaction was demonstrated for TNT. For the first time, it was shown directly that the course of chemical reactions in cast and pressed TNT differs fundamentally.

The assumption on the absence of a direct relation between the chemical reaction zone and the pressure was made based on the comparison of the data on the duration of pressure and conductivity peaks obtained at the detonation of HMX, RDX and PETN. The pressure is not linked directly with the reaction zone, it does not trace the state of matter in that zone, it is insensitive to the chemical processes. Increase of the charge diameter and length results in the slowing down of the rarefaction rather than in the increase of the duration of the reaction zone. The CJ point defined as the point where the mass velocity is equal to the local speed of sound and the ending of the chemical reaction zone can be separated in space. The detected weak influence of the density on the chemical peak duration can be explained within the framework of the proposed hypothesis, and it indicates that the cinetics is "detached" from mechanical parameters.

The diagnostics of the chemical peak by the electric conductivity opens wide possibilities for the investigation of the reaction zone and for the development of a theory of hot spot ignition. Presently, the conductivity method is a powerful tool for the investigation of the chemical reaction zone at detonation. This method provides information on the course of chemical transformations with high temporal resolution. It is suitable for the diagnostics of the matter state in the chemical peak and for the investigation of non-classical and overdriven regimes.

### Acknowledgements

This work was supported by the Russian Foundation for Basic Research (project no. 15-03-01039a).

- 
- [1] Loboiko B.G., Lubyatinsky S.N. *Combust. Expl. Shock Waves*, 2000, **36**, 716.  
 [2] Zel'dovich Ya. B., Kompaneets A. S. *Theory of Detonation*. New York: Academic Press, 1960.

- [3] Fedorov A. V., Men'shikh A. V., and Yagodin N. B. *Khimicheskaya Fizika (Chemical Physics)*, 1999, **18(11)**, 64 (in Russian).  
 [4] S. D. Gilev and A. M. Trubachev, in *Proceedings of the*

- 12th international Detonation Symposium, San Diego, CA (2002), Paper No. ONR333-05-2, p. 240.
- [5] S. D. Gilev, Doctoral dissertation, Institute of Hydrodynamics, Novosibirsk, Russia, 2009.
- [6] A.N. Dremin, S.D. Savrov, and V.S. Trofimov, K.K. Shvedov: Denotation Waves in Condensed Matter (Nauka, Moscow, 1970).
- [7] Titov V.M., Anisichkin V.F., and Mal'kov I.Yu. *Fizika Gorenia i Vzryva (Combustion, Explosion and Shock Waves)* 1989, **25(3)**, 117 (in Russian).
- [8] Yushi Wen, Chaoyang Zhang, Xiangui Xue and Xinping Long, *Phys. Chem. Chem. Phys.*, 2015, **17**, 12013. DOI: 10.1039/c5cp00006h
- [9] Satonkina N.P. *J. App. Phys.*, 2015, **118**, 245901-1. doi: 10.1063/1.4938192
- [10] Satonkina N.P. *Fizika Gorenia i Vzryva*, 2016, **52**, 1. (in Russian)
- [11] K. Tanaka, Detonation Properties of Condensed Explosives Computed Using the Kihara-Hikita-Tanaka Equation of State. National Chemical Laboratory for Industry, Tsukuba Research Center (1983).
- [12] V. N. Korobenko, A. I. Savvatimskiy and R. Cheret, *International Journal of Thermophysics*, **20**, 1247 (1999).
- [13] V. N. Korobenko, A. I. Savvatimskiy, Temperature: Its Measurement and Control in Science and Industry. New York, **7**, 783 (2003).
- [14] E. R. Prueel, D. I. Karpov, and N. P. Satonkina, in *Proceedings of the XV International Detonation Symposium* (2014), p. 814.
- [15] N. P. Satonkina and A. A. Safonov, *J. Eng. Thermophys.-Russ.* **18(2)**, 177 (2009). doi: 10.1134/S181023280902009X
- [16] N. P. Satonkina and I. A. Rubtsov, *Tech. Phys.* **61(1)**, 142 (2016). doi: 10.1134/S1063784216010175
- [17] A.P. Ershov, N.P. Satonkina. *Combust. Expl. Shock Waves*, **45(2)**, 205 (2009).
- [18] O. N. Breusov, *Khim. Fiz.* 21(11), 110 (2002) (in Russian).
- [19] V. F. Anisichkin, *Combust., Explos. Shock Waves* 30(5), 667 (1994).
- [20] V. F. Anisichkin, *Combust., Explos. Shock Waves*. 43(5), 580 (2007).
- [21] Ershov A. P., Satonkina N. P., and Ivanov G. M. *Russian Journal of Physical Chemistry B*, 1999, **1(6)**, 588.
- [22] Kobylkin I. F., Solov'ev V.S., Boiko M. M. *Fizika Gorenia i Vzryva (Combustion, Explosion and Shock Waves)* 1983, **4**, 120 (in Russian).
- [23] L. V. Al'tshuler, G. S. Doronin, V. S. Zhuchenko, *Combust. Expl. Shock Waves* **25(2)**, 209 (1989).
- [24] Ershov A.P., Satonkina N.P. *Combust. Flame*, 2010, **157**, 1022.
- [25] Fedorov A. V. *Khimicheskaya Fizika (Chemical Physics)*, 2005, **24(10)**, 13 (in Russian).
- [26] A. P. Ershov, A. O. Kashkarov, E. R. Prueel, N. P. Satonkina, V. V. Sil'vestrov, A. S. Yunoshev, and A. V. J. *App. Phys.*, 2016, **119**, 075903-1. DOI: 10.1063/1.4942359
- [27] Fedorov A.V., Mikhailov A.L., Antonyuk L.K., Nazarov D.V., Finyushin S.A. *Combust. Expl. Shock Waves*, 2012, **48**, 302.
- [28] A.P. Ershov, N.P. Satonkina. *Combust. Expl. Shock Waves*, 2009, **45**, 205.
- [29] A. P. Ershov, N. P. Satonkina, O. A. Dibirov, S. V. Tsykin, and Yu. V. Yanilkin. *Combust. Expl. Shock Waves*, 2000, **36**, 639.
- [30] Pineau N., Soulard L., Los J. H., Fasolino A. *Journal of Chemical Physics*. 2008. V. 129. P. 024708-1 – 024708-8.
- [31] A.V. Rode, S.T. Hyde, E.G. Gamaly, R.G. Elliman, D.R. McKenzie, S. Bulcock, *Appl. Phys. A*, V. 69, P. S755, 1999.
- [32] A. Zani, D. Dellasega, V. Russo, M. Passoni, *CARBON*, **56**, May 2013, p. 358-365.
- [33] Vasil'ev A.A., Pinaev A.V. *Combustion, Explosion, and Shock Waves*. 2008. **44(9)**. p. 317-329.
- [34] Ornellas D. L. Calorimetric Determination of the Heat and Products of Detonation for Explosives: October 1961 to April 1982, LLNL, UCRL-52821 (1982).
- [35] Nomura Y., Kawamura R. Soot derived from the detonation of a trinitrotoluene charge // *Carbon*. 1984. **22(2)**, p. 189-191.
- [36] Greiner N. Roy, Phillips D. S., Johnsov J. D., Volk Fred. *Nature*. 1988. **333**, 2 June. p. 440-442.